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COAL PARTICLE DISINTEGRATION AT ELEVATED TEMPERATURES

A REPORT PREPARED

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ABSTRACT

The impact of process variables on the disintegration of coal particles in the presence of a solvent at elevated temperatures was explored with a novel view cell. The apparatus, equipped with sapphire windows, permitted direct visual observation of 100 um particles up to 700 K and 100 bar. As the focus of this work was to identify disintegration mechanisms, disintegration rates per se were not measured. The impact of each variable was assessed through changes in particle morphology over a fixed reaction period. Only presaturation of coal particles with a hydroaromatic solvent coupled with agitation was found to affect the basic disintegration mechanism which is characterized by the cleavage of micron and submicron fragments from parent particles as dissolution reactions progress. These findings are consistent with a physiochemical mechanism for coal particle disintegration where reagent starvation arises within coal particles. As coal particles are unstable and disintegrate rapidly in hydrogenation reaction environments at temperatures greater than 700 K, the potential role of coal particles as a catalyst support for coprocessing or heavy oil upgrading processes is questioned.

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1. INTRODUCTION

The disintegration of coal particles is a crucial first step in coprocessing and coal liquefaction reaction environments, and is a matter of concern for applications where coal particles are to be used as a catalyst support. Despite its importance, little is known about this phenomenon and few direct measurements have been reported in the open literature. Pozzobon et al. (1990) conducted some preliminary experiments with a capillary view cell, in the absence of catalytic and mixing effects, and proposed a physiochemical model for particle disintegration.

In rough outline, their model proposes that small reagent molecules diffuse into the sub-micro pores of coal particles where they react rapidly with coal constituents to produce molecular species of intermediate density. These latter species are further proposed to be too large to diffuse out of the pores and the resulting pressure rise within the pores causes the particles to fracture. The model is supported by experimental evidence. For example, Pozzobon et al. (1990) observed micron and submicron sized fragments drifting away from parent particles when suitable reagents were present in the reaction environment. The proposed mechanism is also consistent with extant coal dissolution kinetic studies, where particle size is found to be a variable of secondary importance. Particles can be completely disintegrated at minimal conversion.

In the present work, the impact of agitation, solvent saturation, and catalyst impregnation on the mechanism or rate of particle disintegration is explored. Questions addressed include: do impregnated catalysts help or hinder the disintegration process, does saturation of coal particles with solvent (swelling) alter the disintegration mechanism, does agitation accelerate the disintegration process? We also question the suitability of coal particles per se as catalyst supports for hydrocarbon hydrogenation processes.

2. EXPERIMENTAL

2.1 MATERIALS

The physical properties of the gases and solvents, obtained from various suppliers, are given in Table 2.1. Blind Canyon and Battle River coal samples were supplied by the Pittsburgh Energy and Fuels Research Centre and by Energy, Mines and Resources Canada respectively. Proximate and ultimate analyses for the coals are shown in Tables 2.2 and 2.3.

Table 2.1 Physical properties of gases and solvents

	hydrogen	nitrogen	tetralin	hexadecane
purity, %			99	97
molecular formula	H_2	N_2	$C_{10}H_{12}$	$C_{16}H_{34}$
molar mass	2.016	28.013	132.22	226.45
melting point, K				291
boiling point, K			481	560
critical temperature, K	33	148	719	722
critical presssure, MPa	1.29	3.39	3.5	1.4

Table 2.2 Blind Canyon coal analysis

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF
% moisture	5.20			
% ash	13.17	13.89		
% volatile	39.23	41.38	48.05	47.30
% fixed carbon	42.40	44.73	51.95	52.70
ULTIMATE ANALYSIS				
% carbon	66.15	69.78	81.04	82.35
% hydrogen	4.80	5.06	5.88	5.97
% nitrogen	1.21	1.28	1.49	1.51
% total sulfur	0.45	0.47	0.55	
% oxygen (diff)	9.02	9.52	11.06	10.17

Table 2.3 Battle River coal analysis

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF
% moisture	26.01		
% ash	10.53	14.23	
% volatile	27.06	36.57	42.64
% fixed carbon	36.40	49.20	57.36
ULTIMATE ANALYSIS			
% carbon	47.13	63.70	74.27
% hydrogen	3.25	4.39	5.12
% nitrogen	0.95	1.28	1.50
% sulfur	0.40	0.54	0.63
% oxygen (diff)	11.73	15.86	18.48

2.2 EQUIPMENT

All experiments were performed in a 50 cm^3 sandwich style cell designed for a maximum working pressure of 200 bar at 700 K. The cell system is constructed of 316 stainless steel and the cell body is machined into a block of stainless steel. The sapphire windows at both ends are sealed and cushioned by graphite shims and clamped in place by stainless steel cover plates. The studs that secure the whole assembly include spring washers which compensate for differential thermal expansion effects. The cell is equipped with ten ports. During this study, three are used for pressure and temperature monitoring, and a rupture disc connection, and two for fluid inlet and outlet. The cell was manufactured by D. G. Robinson and Associates and a schematic is shown in Figure 1.

While the structure of the cell permitted direct observation of disintegrating coal particles, it also imposed restrictions and limitations on cell performance. The cell walls and trace constituents of the graphite gaskets are known to catalyse hydrogenation/dehydrogenation reactions which result in solvent degradation. This accentuates the thermal instability of the solvents and consequently the solvents are not pure under reaction conditions. The impact of this phenomenon on our results is thought to be minimal. Differential thermal expansion problems imposed greater restrictions and consequently heating and cooling rates were limited to 0.06 K/s, as shown in Figure 2, to avoid over stressing the sapphire windows. Even so, the experimental program was cut short by a window failure during a cooling cycle. Despite these limitations over all cell performance was found to be satisfactory.

2.3 CELL OPERATING PROCEDURE

During a typical experiment, four or five coal particles and solvent are loaded into the cell, which is then depressurized with an aspirator to remove air. The cell is then repressurized

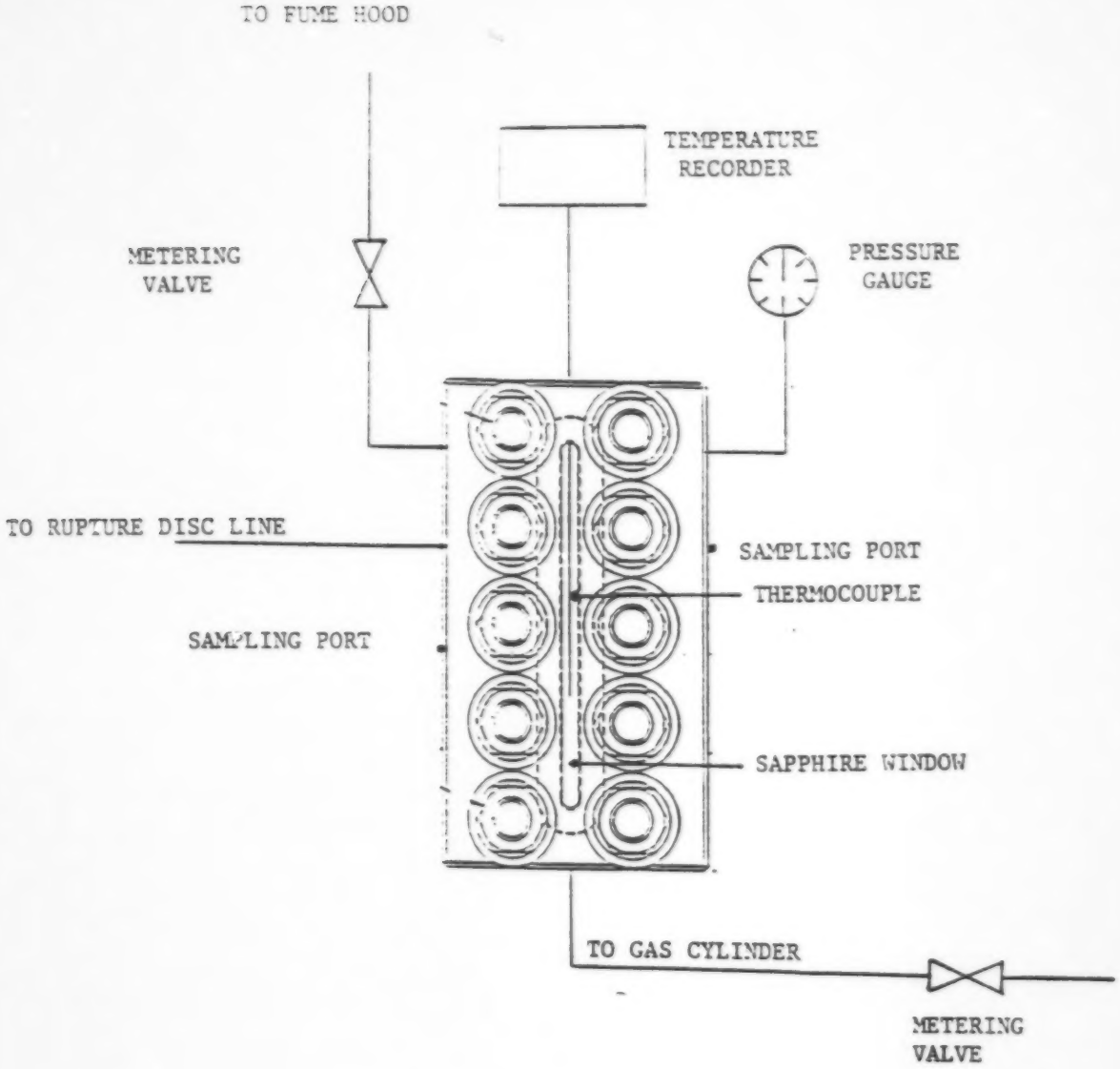

Figure 1. Apparatus

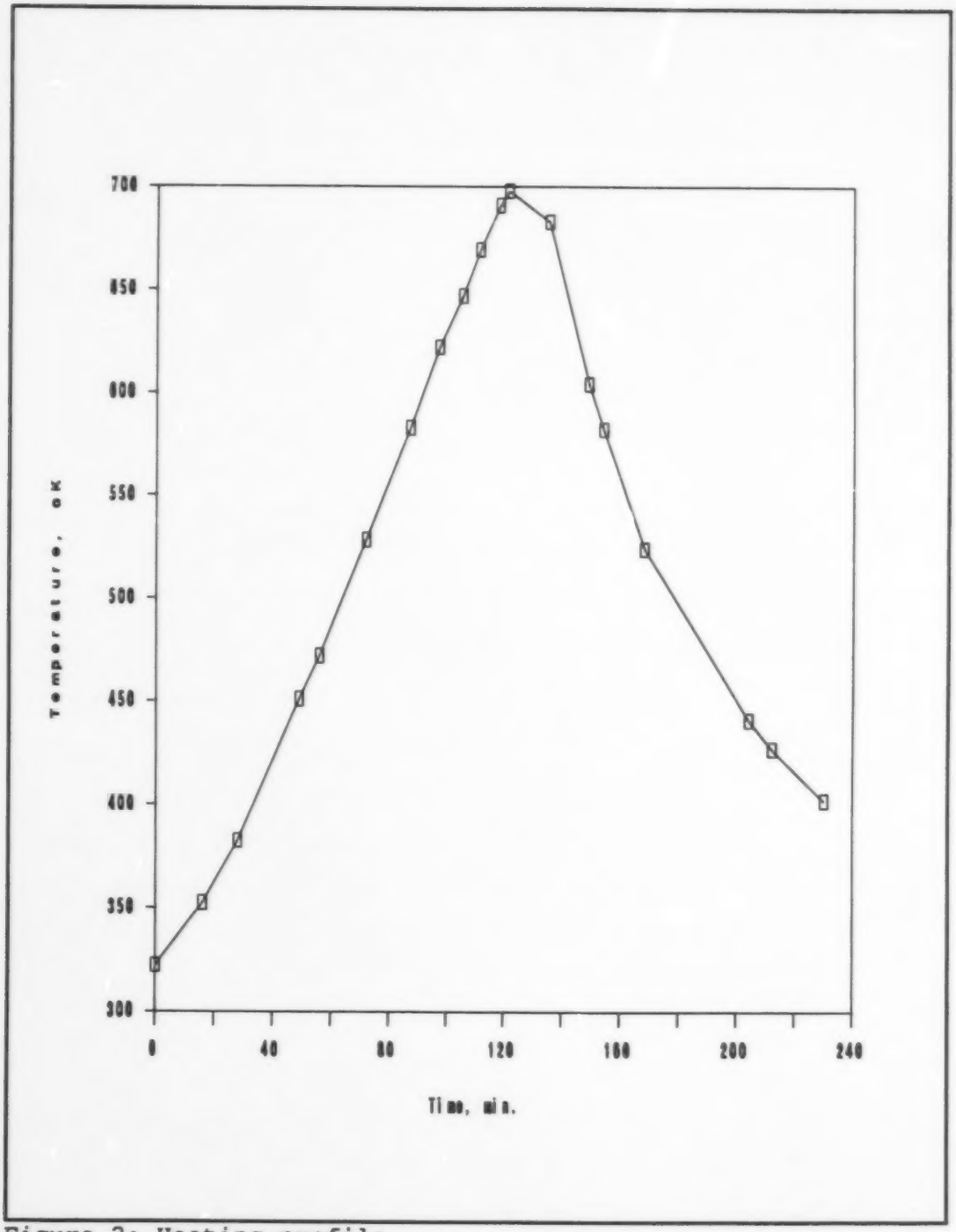

Figure 2: Heating profile

with gas. During experiments with mixing, gas bubbles with a 2.4 mm diameter are continually fed through the base of the cell and gas is bled from the top to maintain a target pressure. During experiments without mixing, the reactor is sealed and allowed to reach a target pressure. In all cases, the cell is heated to 700 K and particle disintegration was recorded on video at 9 x magnification.

2.4 COAL-CATALYST PREPARATION

Coal particles were impregnated with catalyst using a method developed by Dukhedin-Lalla et al., 1991 a & b. Briefly, samples of dried coal particles ranging in size from 1 to 3 mm were soaked in a 10 wt % iron sulphate solution over night. The iron sulphate, supplied by Fisher Scientific was 99.1 wt % pure. Once treated, the coal samples were dried in a desiccator under vacuum for 48 h. Dukhedin-Lalla et al. (1991 b) showed that with this preparation method metal sulphate catalysts were dispersed homogeneously throughout the coal particles at a concentration of 1 to 2 wt %.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 SUMMARY OF EXPERIMENTS AND VARIABLES

A matrix of experiments was established involving the following variables and levels: coal type (Blind Canyon, Battle River), gas type (hydrogen, nitrogen), solvent type (tetralin, hexadecane), catalyst (iron sulphate, none), initial gas pressure (500, 800, 1000), mixing (bubble injection, none), and solvent saturation of particles (yes, no) ie. for some experiments the coal particles were let stand over night in solvent under pressure but at room temperature. A total of 18 experiments were performed before the cell failed. The conditions for these experiments are summarized in Table 3.1. In all other respects the operating conditions for these experiments were identical. Photomicrographs associated with each experiment are shown in Figures 3 to 30 and an edited videotape for experiment 9 is available on request.

Table 3.1: Summary of experimental programme

No.	Coal	Pres. init/ final (MPa)	Catalyst	particle satura-tion	Solvent	Gas	Mix-ing
1	Blind Canyon	3.45/ 7.79	no	not sat.	tetralin	H2	none
2	Blind Canyon	3.45/ 7.58	no	not sat.	tetralin	N2	none
3	Battle River	3.45/ 7.03	no	not sat.	tetralin	H2	none
4	Battle River	3.45/ 7.58	no	not sat.	tetralin	N2	none
5	Blind Canyon	3.45/ 7.58	yes	not sat.	tetralin	H2	none
6	Battle River	3.45/ 7.58	yes	not sat.	tetralin	H2	none
7	Battle River	3.45/ 7.24	yes	sat.	tetralin	H2	none
8	Battle River	5.50/ 9.65	yes	not sat.	tetralin	H2	none
9	Blind Canyon	5.50/ 11.03	yes	not sat.	tetralin	H2	none
10	Blind Canyon	6.90/ 11.72	yes	not sat.	tetralin	H2	none
11	Battle River	6.90/ 11.72	yes	not sat.	tetralin	H2	none
12	Blind Canyon	6.90/ 11.03	yes	sat.	tetralin	H2	none
13	Blind Canyon	5.50/ 8.27	yes	not sat.	tetralin	H2	yes
14	Battle River	6.90/ 7.58	yes	not sat.	tetralin	H2	yes
15	Battle River	6.90/ 7.58	yes	sat.	tetralin	H2	yes
16	Battle River	6.90/ 10.2	yes	sat.	tetralin	H2	none
17	Blind Canyon	6.90/ 8.96	yes	sat.	hexadec-ane	H2	none
18	Blind Canyon	6.90/	yes	not sat.	hexadec-ane	H2	none

Figure 3. Pre-reaction
run #1

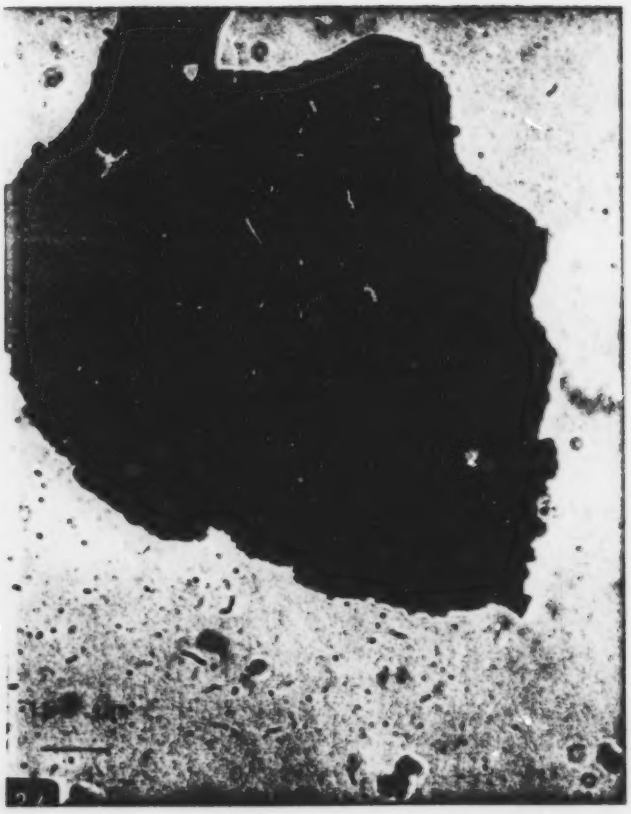

Figure 4. Post-reaction
Blind Canyon Coal
Hydrogen & Tetralin
Pressure= 3.45 Mpa
run #1

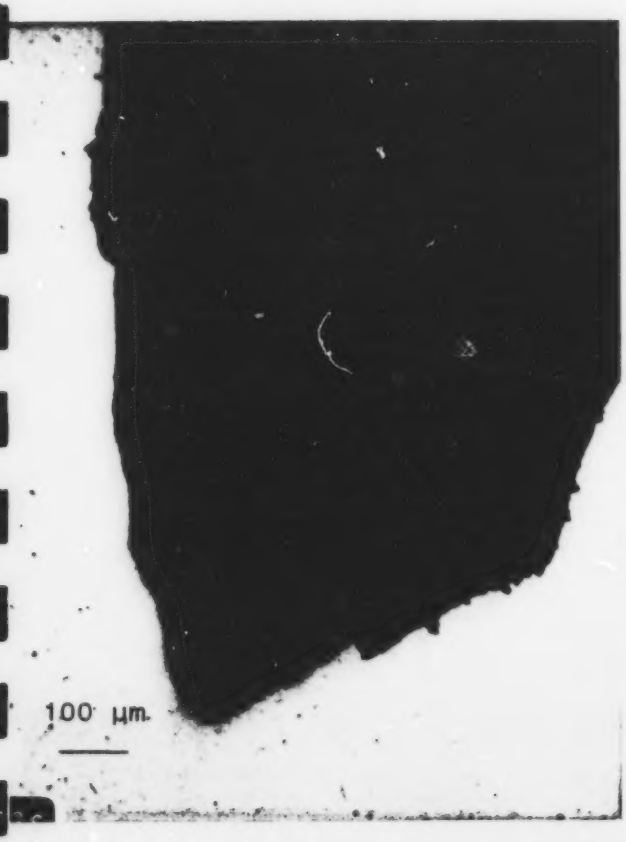

Figure 5. Pre-reaction
run #2

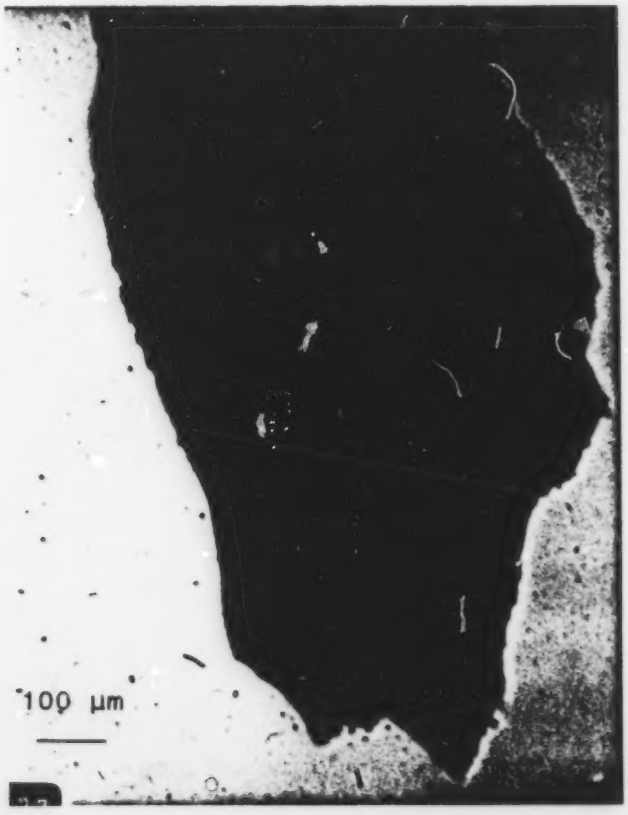

Figure 6. Post-reaction
Blind Canyon Coal
Nitrogen & Tetralin
Pressure= 3.45 Mpa
run #2

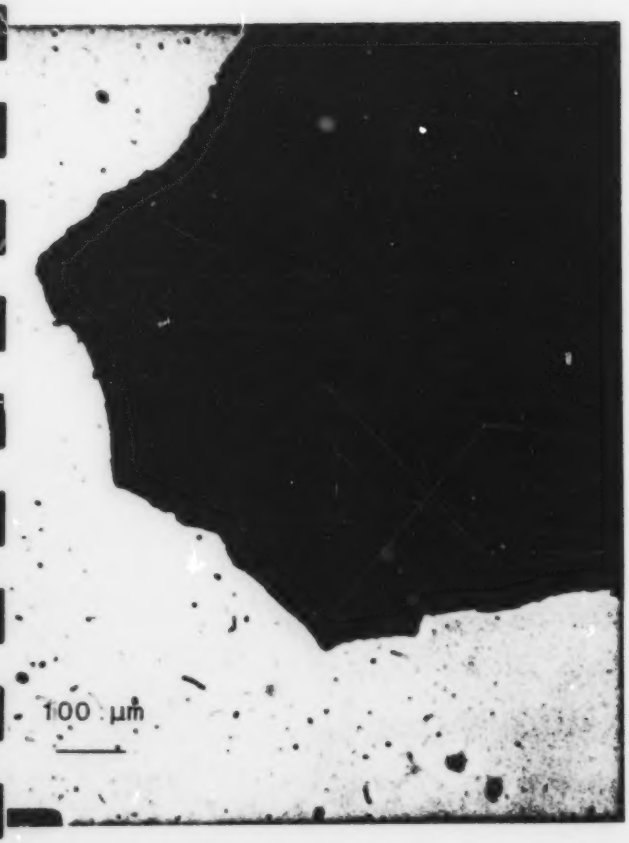

Figure 7. Pre-reaction
run #3

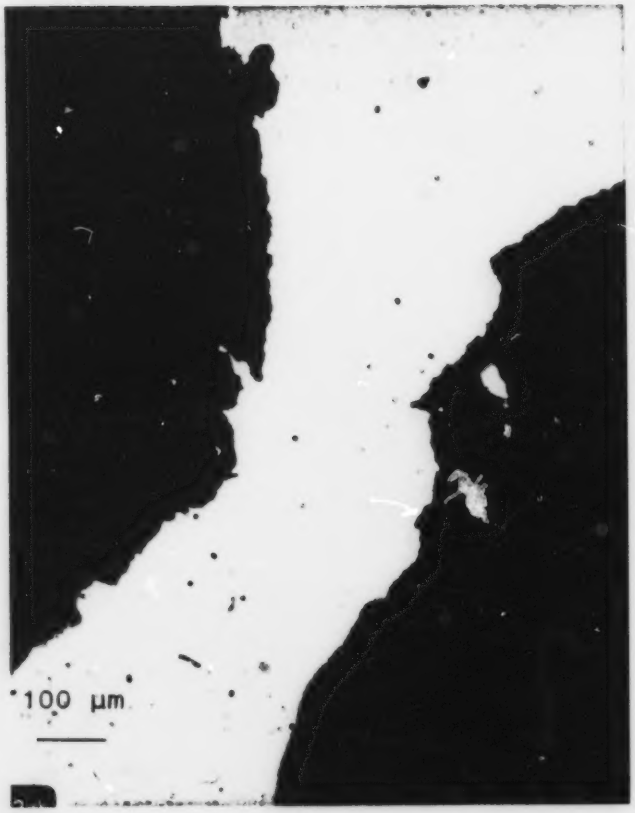

Figure 8. Post-reaction
Battle River Coal
Hydrogen & Tetralin
Pressure= 3.45 Mpa
run #3

Figure 9. Pre-reaction
run #4

Figure 10. Post-reaction
Battle River Coal
Nitrogen & Tetralin
Pressure= 3.45 Mpa
run #4

Figure 11. Pre-reaction
run #5

Figure 12. Post-reaction
Blind Canyon Coal+Catalyst
Hydrogen & Tetralin
Pressure= 3.45 Mpa
run #5

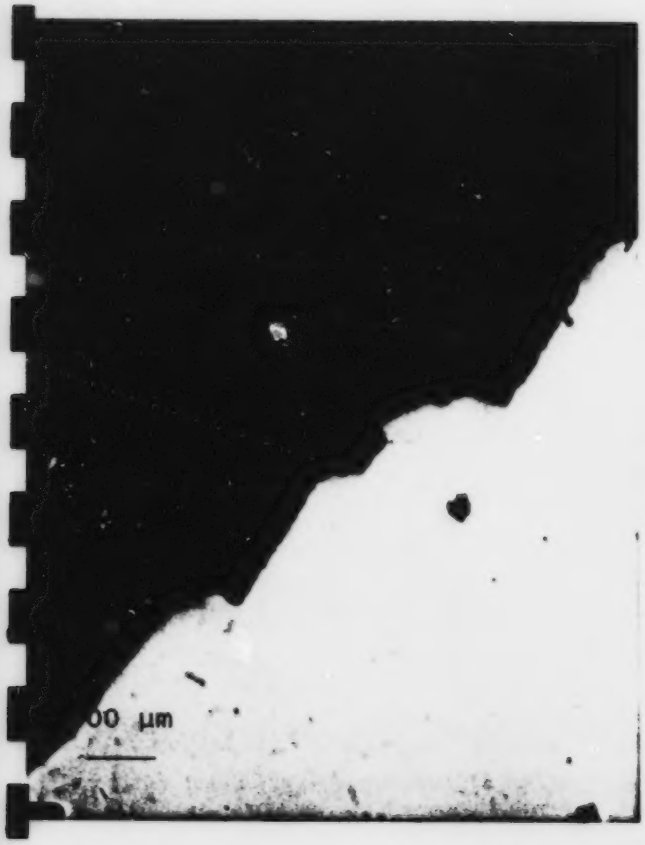

Figure 13. Pre-reaction
run #6

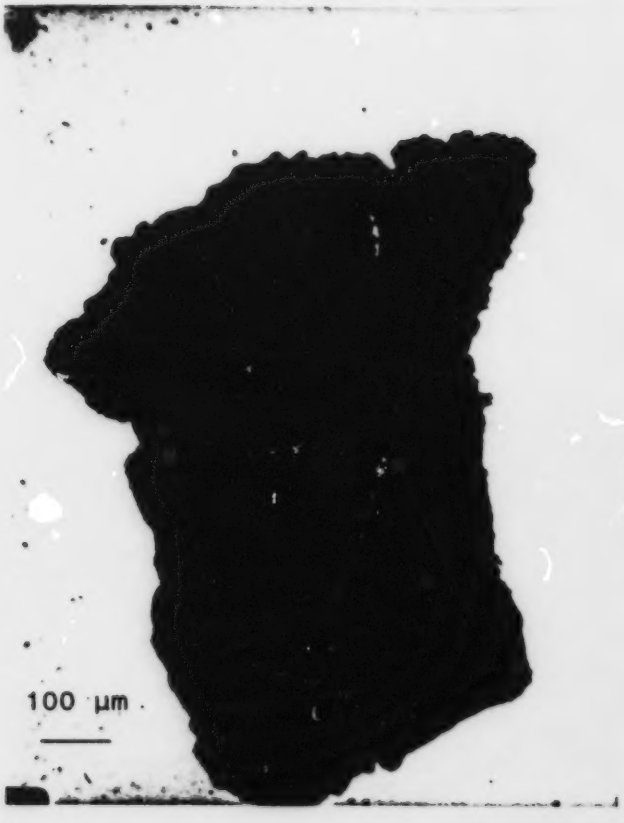

Figure 14. Post-reaction
Battle River Coal+Catalyst
Hydrogen & Tetralin
Pressure= 3.45 Mpa
run #6

Figure 15. Pre-reaction
run #7

Figure 16. Post-reaction
Battle River Coal+Catalyst
Hydrogen & Tetralin
Pressure= 3.45 Mpa
Saturated
run #7

Figure 17. Pre-reaction
run #8

Figure 18. Post-reaction
Battle River Coal+Catalyst
Hydrogen & Tetralin
Pressure= 5.5 Mpa
Run #8

Figure 19. Pre-reaction
run #9

Figure 20. Post-reaction
Blind Canyon Coal+Catalyst
Hydrogen & Tetralin
Pressure = 5.5 Mpa
Run #9

Figure 21. Pre-reaction
run #10

Figure 22. Post-reaction
Blind Canyon Coal+Catalyst
Hydrogen & Tetralin
Pressure = 6.9 Mpa
Run #10

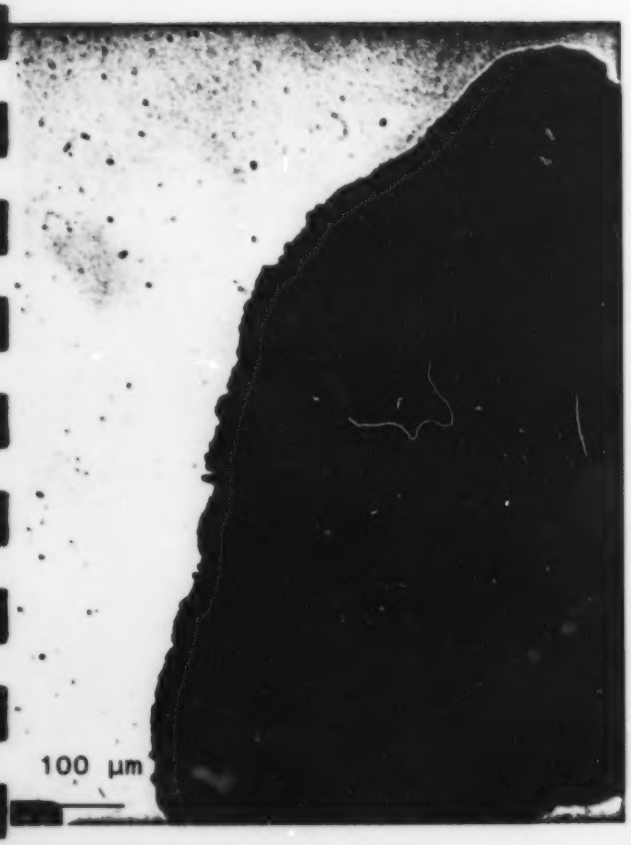

Figure 23. Pre-reaction
run #11

Figure 24. Post-reaction
Battle River Coal+Catalyst
Hydrogen & Tetralin
Pressure = 6.9 Mpa
Run #11

Figure 25. Pre-reaction
run #12

Figure 26. Post-reaction
Blind Canyon Coal+Catalyst
Hydrogen & Tetralin
Pressure= 6.9 Mpa
Saturated
Run #12

Figure 27. Post-reaction
Battle River Coal+ Catalyst
Hydrogen & Tetralin
Pressure= 6.9 Mpa
Mixing
Run #14

Figure 28. Post-reaction
Battle River Coal+Catalyst
Hydrogen & Tetralin
Pressure= 6.9 Mpa
Saturated
Mixing
Run #15

Figure 29. Post-reaction
Battle River Coal+ Catalyst
Hydrogen & Tetralin
Pressure= 6.9 Mpa
Saturated
Run #16

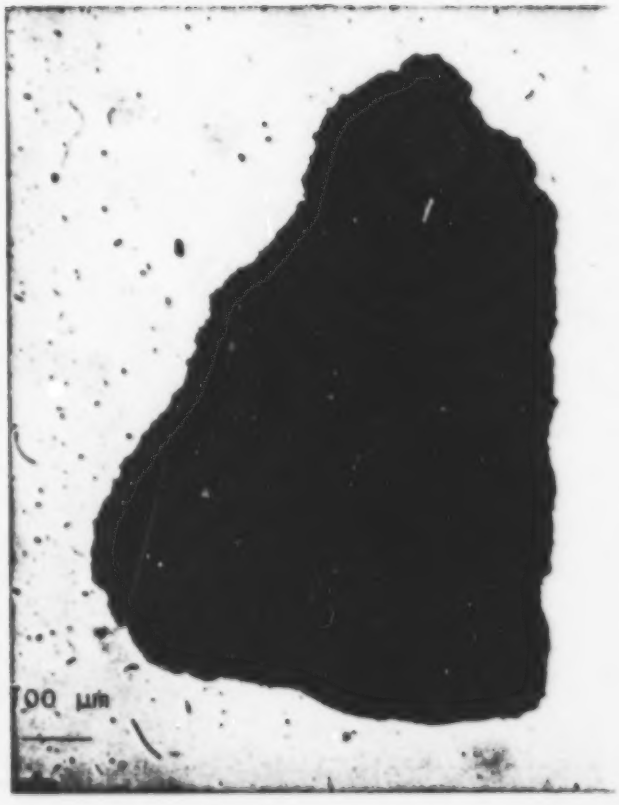

Figure 30. Post-reaction
Blind Canyon Coal+Catalyst
Hydrogen & Hexadecane
Pressure= 6.9 Mpa
Saturated
Run #17

3.2 AN OVERVIEW OF THE EXPERIMENTAL RESULTS

In general, it is worth noting that, Battle River coal is more reactive than Blind Canyon coal under the reaction conditions employed. Thus coal type is of importance in determining the rate of particle disintegration. However, this variable is of less importance than some of the variables considered below.

The first four experiments re-examine the role of hydrogen in the particle disintegration process. The results, summarized in Figures 3 to 10, confirm previous findings concerning the key role played by hydrogen (Pozzobon et al., 1990). For both coals, the post reaction particle morphology is much rougher and the particles exhibit a greater extent of erosive breakage when hydrogen is present in the reaction environment. We also observed that by increasing the initial hydrogen pressure that the extent of particle erosion is enhanced. This finding highlights a mass transfer limitation and is in agreement with previous findings. For example, compare Figures 24 and 6 or 22 and 4.

Comparison of the results of experiments 1 and 3 with 5 and 6, depicted in Figures 4, 8, 12 and 14 respectively, clearly shows that added catalyst has little impact on the disintegration process as there is little difference in the post reaction particle morphologies or particle sizes for both coal types with or without catalyst. Ruberto, Tarrent, Rottendrof, Debyshire and others have reported that the main contribution of a catalyst during coal hydrogenation processes is the hydrogenation of solvent soluble species. Our results are certainly consistent with this finding, as the dispersed iron sulfate catalyst does not play a role in coal particle disintegration.

Soaking coal particles in tetralin appears to accelerate the disintegration process, for example, the post reaction particles from experiment 7 (Figure 16) are more eroded than those of experiment 6 (Figure 14). By contrast, the solvent hexadecane appears to retard particle disintegration. The post reaction particles from experiment 17 (Figure 30) appear almost unreacted

when compared with those of experiment 12 (Figure 26). Alaphatic solvents appear to retard particle disintegration despite their higher hydrogen solubility (Shaw, 1988). Thus soaking per se is not an important variable but soaking in an aromatic/hydroaromatic solvent does accelerate particle disintegration.

The maximum shear rate obtained through the continual injection of 2.4 mm diameter hydrogen bubbles at the base of the cell is low and insufficient to cause mechanical breakage of unreacted coal particles. However, it is sufficient to rupture fluid films and fluid drops as described elsewhere (Hatikiriakos et al., 1990 a & b). A comparison of the results from experiments 11 (Figure 24) and 14 (Figure 27) reveals that in the absence of solvent saturation agitation merely breaks off the eroded tips of the coal particles, ie. post reaction particles from experiment 11 remain large but possess rough morphologies while those from experiment 14 are apparently smoother but somewhat smaller. The sequence of experiments 14, 15, 16 highlight the combined effect of solvent saturation and mixing. In the absence of solvent soaking but in the presence of agitation post reaction particles remain large (Figure 27). In the absence of agitation but in the presence of solvent saturation the particles also remain large (Figure 29). However, when both are present, the post reaction particles are very much smaller and exhibit an extremely rough morphology (Figure 28).

To summarize, the conditions most favourable to coal particle disintegration include: high pressure hydrogen gas and presaturation of particles with an aromatic/hydroaromatic solvent, coupled with agitation. Impregnated catalysts have no impact on disintegration rates where as alaphatic solvents and inert gases appear to inhibit particle disintegration.

3.3 MECHANISMS FOR COAL PARTICLE BREAK UP

Translation of the phenomenological evidence above into mechanisms for particle disintegration is straight forward. Particle disintegration is characterized by mass transfer limited erosive breakage where molecular hydrogen is the principal reacting species. The basic model remains unchanged from our previous publication on this topic (Pozzobon et al., 1990). However, this model is incomplete and must be augmented because it fails to include the roles played by solvents and agitation.

Presaturation of a coal particle with a hydroaromatic solvent and hydrogen facilitates the penetration of these species through to the particle core via diffusion through pores or directly through the coal matrix (cf. Larsen and Lee, 1983). If the particle is then heated, these species react with the coal matrix in much the same way as they do at the surface and the particle structure is weakened. As some macerals are more readily penetrated with solvents or are more reactive than others, coal particles quickly become an agglomeration of sub-particles held together by thin fluid films. Under mild agitation, these films are ruptured and the much finer sub-particles which result then break up according to the basic mechanism. In the presence of an unsuitable solvent, diffusion processes and hydrogenation reaction rates are reduced and particle disintegration is retarded. With this adendum the coal particle disintegration model appears to be complete.

3.4 SUITABILITY OF COAL PARTICLES AS A CATALYST SUPPORT

The experiments reported in this paper mimic the behaviour of a slow preheater for hydrogenation processes. More typically the heat up time would be six minutes rather than two hours. Thus the impact of mass transfer effects on particle disintegration would be even more pronounced and the particles would be more durable at elevated temperatures than indicated by the experiments. As particle disintegration rates accelerate at temperatures greater than 700 K, particles per se do not persist beyond five to ten

minutes at elevated temperatures in hydrogenation reaction environments. In such cases, the particles merely act as a catalyst dispersant rather than as a support, and other dispersant methods may prove equally effective. The application of coal particles as a catalyst support must be restricted to reaction environments where the reaction time is short, the reaction temperature is relatively low, the hydrogen partial pressure is low and where the hydrocarbon liquids are primarily alaphatic in nature.

4. CONCLUSIONS

Coal particle disintegration in solvents at elevated temperatures is characterized by the erosive cleavage of micron and submicron particle fragments from parent particles. The rate of particle disintegration is limited by molecular hydrogen transfer to/within coal particles but is unaffected by the presence of impregnated catalysts. Saturation of particles with a hydroaromatic solvent coupled with agitation contributes a complimentary breakage mechanism where large reacting coal particles are cleaved into random sized sub-particles which are in turn subject to erosive cleavage. As coal particles are not durable at elevated temperatures, they can act more readily as dispersants for catalysts than as catalyst supports.

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